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Leaching flue dust

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LEACHING FLUE DUST

BY

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A

THESIS

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Leaching Flue Dust.

INTRODUCTION.

The usual method of treatment has been to charge the "flue dust"into reverberatories and smelt it with the regular charge of calcined ore.There was a consequent cost of handling and a serious loss thru furnace draft and boiling,due to the fine state of division of the material and the presence of sulphates,acid,and moisture.

The object of thei paper is to treat this material by some leaching process,which will eliminate the above enumerated losses,and at the same time present the finished product at a lower cost,and with a higher extraction per ton,than has previously been done by other processes.

An analyses of the "flue dust"showed the following elements present:

Copper	4.50%
Zinc	.665%
Iron	30.82%
Lead	I.I4%
Sulphur	9.075%
Silicia	23.3%

Determinations were made with all manner of acids and salts,and combinations of acids and salts,with a view of obtaining a high extraction.

EXPERIMENTAL RESULTS.

Leaching with Water

Sample	Days leached	Leaching Sol.	% Cu.Extract.
I-5gms.	I	water I00cc.	I.95
2- "	2	" "	I.95
3- "	3	" "	2.04
4- "	4	" "	I.95
5- "	5	" "	2.I3

Roasting "flue dust" in a muffle furnace at a temp. of 650° C for one hour. Subsequently leaching Ist. with water,2rd. with acid.

Ist.

Sample	Days leached	Leaching Sol.	%Cu.Extract.
I-I0gma.	I	water Ioo cc.	None
2- "	2	" "	"
3- "	3	" "	Trace
4- "	4	" "	"

2rd.

Sample	Days leached	Leaching solut.	% Cu. Ext.
I-Iogms.	I	I% H_2SO_4 by vol.	I5.2
2- "	2	" " " "	I5.7
3- "	I	3% " " "	I6.2
4- "	2	" " " "	I7.4

Sulphate rocess.

Sample	Days leached	Leaching solut.	% Cu. Ext.
I-Iogms.	I	I H_2SO_4 by vol.	34.9
2- "	2	" " " "	34.9
3- "	6	" " " "	38.6
4- "	8	" " " "	39.3
5- "	I	3% " " "	43.3
6- "	2	" " " "	4I.2
7- "	6	" " " "	48.8
8- "	8	" " " "	47.8
9- "	8	5% " " "	46.7

Sulphate Process by Agitation.

Sample	Hrs. Agit.	Leaching solut.	% Cu. Ext.
I-30 gms.	5	3% H_2SO_4 by vol.	40.I
2- "	5	5% " " "	44.I
3- "	8	3% " " "	47.I
4- "	8	5% " " "	49.7

Pulp of sample #4 leached for three days with a 5% solution of NH_4Cl resulting in a further extraction of 20.3%. Total extraction 70%.

Leaching "Flue Dust" with HCl.

Sample	Days leached	Leaching solut.	% Cu. Ext.
I-5gms.	I	2% HCl by vol.	3 O.I
2- "	2	" " " "	32.7
3- "	6	" " " "	33.9
4- "	I	4% " " "	4I.5
5- "	2	" " " "	45.5
6- "	6	" " " "	46.8

Leaching "Flue Dust"with HNO_3

Sample	Days leached	Leaching solut.	% Cu. Ext.
I-5gms.	I	2% HNO_3 by vol.	30.0
2- "	6	" " " "	32.8
3- "	I	4% " " "	37.I
4- "	2	" " " "	42.4
5- "	6	" " " "	46.2

Agitation with a 5% solution of HN_4OH, after eight hours of agitation with a 5% solution only 4.42% of Cu was extracted.

Leaching "Flue Dust" with Ferric Sulphate.

Sample	Days leached	Leaching solut.	% Cu. Ext.
I-Igm.	3	3% $Fe_2(SO_4)_3$ by vol.	43.I
2-I "	3	" " " "	44.2
3-3gms.	3	5% " " "	42.I
4- "	3	" " " "	43.0
5-5gms.	3	7% " " "	40.0
6- "	3	" " " "	40.5

Sample #4 of the above was taken and the pulp was treated with a 3% solution of H_2SO_4 leaching this pulp for three days. Further extraction of I0.I%. Total 53.I%.

Note. Unless it has otherwise been specified, the total volume of the leaching solution has been I00 cc.

A test to ascertain if the increase in volume of the leaching solution bears any relation to the increase in the percentage extraction.

Sample	Days leached	cc by volume	% Cu. Ext.
I-I0gms.	3	I0	55.8
2- "	3	20	5I.8
3- "	3	40	53.7
4- "	3	60	55.8
5- "	3	80	55.8
6- "	3	I00	48.I
7- "	3	I50	52.4

A 5% solution of H_2SO_4 (hot) was used in the above determination as the solvent. It is evident from this data that a solution by volume which completely saturates the ore to be leached, gives a better, or as good an extraction, as one whose volume is ten times as great. This means a conservation of water, as well as an estimate on the size of a leaching tank required.

Sulphatizing Roast.
Temperature at beginning of roast I50° C.
Temperature at completion of roast 500° C.
Time of roast; one hour.
Pyrite ore was mixed with the "Flue Dust" and the roasted product subsequently leached with a 4% sol. of H_2SO_4. Total volume of solvent 50cc.

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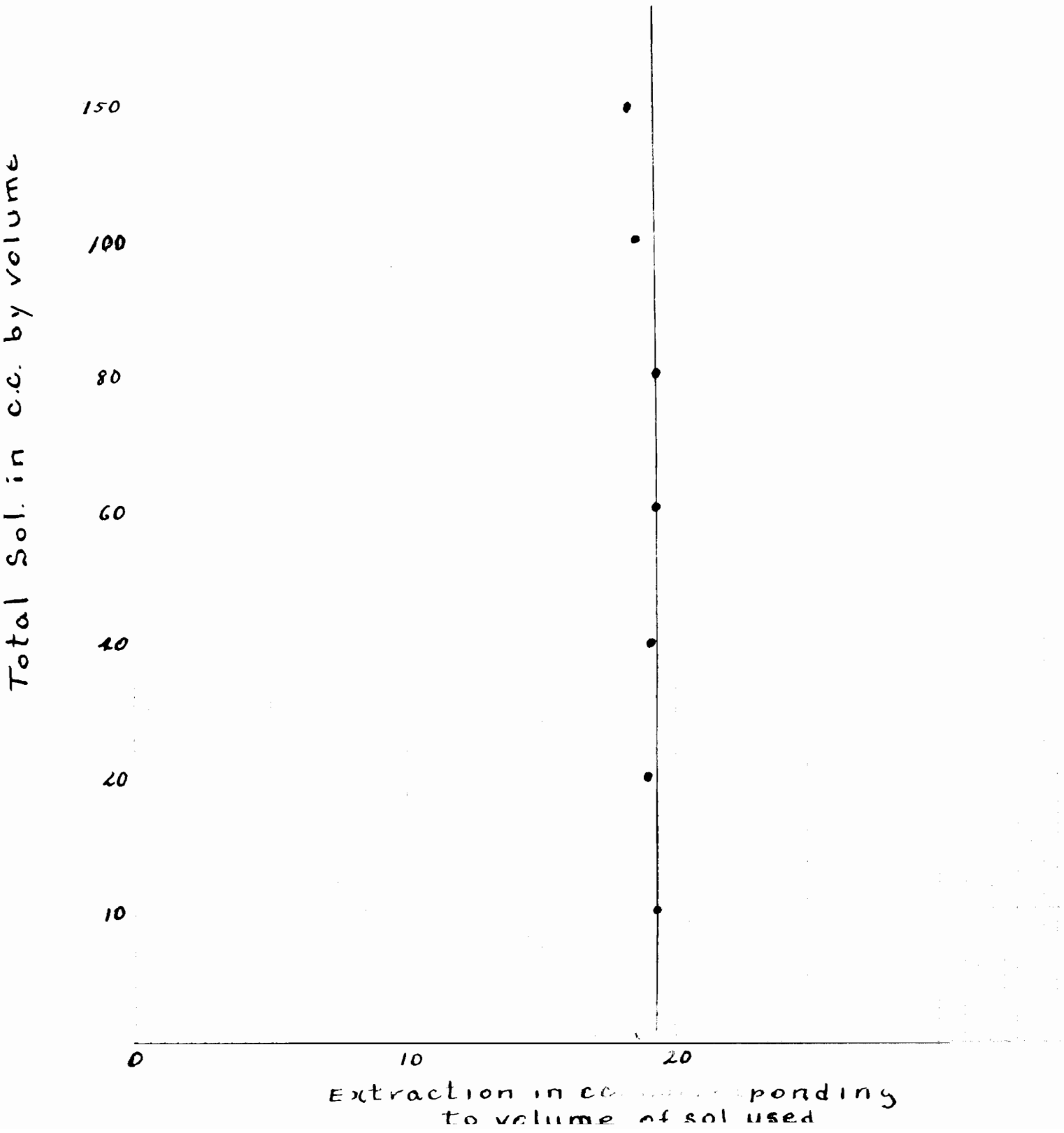

Sample	Flue Dust	Pyrite	Days leached	Cu. Ext. comb.
I	I0 gms.	I0 gms.	4	27.3
2	I5 "	5 "	4	39.3
3	I2 "	8 "	4	35.8
4	5 "	I5 "	4	22.5
5	I8 "	2 "	4	53.7
6	8 "	I2 "	4	33.7

Sample #5 of the roast was treated with a 7% sol. of ferric sulphate (hot) and leached for four days. Copper extraction 37.8%.

From later experiments I found this roast had been more of an oxidizing roast than a sulphatizing having been carried too high. I noticed from this data that a small introduction of sulphur increased the percentage extraction. Other roasts and subsequent leaching with different reagents and with variations in the temperatures of the roast failed to give a higher extraction. These roasts, however, as I later found had always been carried at too high a temperature.

Dottsch Process of Leaching.

Sample	Days	NaCl	Ferrous sulp.	% Cu. Ext.
I	4	.5% by vol.	.5% by vol.	I4.0
2	4	I% " "	I% " "	I5.0
3	4	I% " "	3% " "	I7.2
4	4	2% " "	3% " "	I7.9

Total volume in each case of solvent 50cc.

Some miscellaneous tests with different leaching reagents. In each case ten grams of the "Flue Dust" was used and each test was leached for five days. Raw "Flue Dust" was used and the total volume of the solvent equaled I00cc.

	% Cu Extract.
1. Ammonia sulphate 5% sol. ------	Trace.
2. Ferric sulp. 2% $K_4Fe(CN)_6$ 4% ----	29.0
3. KCN I0% ----- ----------	56.2
4. $Fe_2(SO_4)_3$ 4gms. NH_4SO_4 5cc---------	37.7
5. NH_4Cl 3gms. $Fe_2(SO_4)_3$ 3gms. H_2SO_4 5cc	56.3
6. NaCl 3gms. " 5 " " "	63.2
7. HCN 5% ----------	4I.0
8. KCN 6gms. H_2SO_4 5cc----------	49.0
9. Na_2O_2 4gms. H_2SO_4 7cc (violent)-	60.3
I0. NH_4OH 3cc 2days. Acidified with H_2SO_4 leached for 2days more ----------	40.3
II. NaCl 4gms. H_2SO_4 3cc ----------	39.7

		% CU Extract.
I2.	$KMnO_4$ 3gms. H_2SO_4 6cc.	39.7
I3.	$KMnO_4$ 5 "	23.I
I4.	MnO_2 H_2So_4 4cc	5I.7

The following known processes were tried, none of which gave a satisfactory result.

a.	Mosher-Ludlow Ammonia-Cyanide.	40.I
b.	Neil Sulphate process.	64.9
c.	Ferric Sulphate as tried at Canenea Mexico.	33.3
d.	The Mielberg process.	52.6
e.	Hunt and Douglas process.	68.I
f.	The Elliott process.	44.2
g.	The Laist process.	38.I
h.	Longmaid Henderson process.	66.8
i.	Froelich process.	56.3

After all these processes had been tried and their results were discouraging sulphatizing roasting was again tried this time mixing alternately ores of marcasite, chalcopyrite, and pyrite, with the "flue dust". The temperature of roast being held always below 300° C.

Sulphatizing Roast with Marcasite and Pyrite.

Sample	Marcasite	Flue D.	Days lch.	Leaching s.	% Cu
I	Iogms.	40gms.	6	50cc 4% H_2SO_4	6i.0
2	7 "	"	"	" " "	75.3
3	2 "	"	"	" " "	90.3
4	I "	"	"	" " "	97.5
	Pyrite				
I	I0gms.	"	"	" " "	64.2
2	3 "	"	"	" " "	72.I
3	2 "	"	"	" " "	77.2

The chalcopyrite with the ratio of 2:40 gave almost as good results as the marcasite.

From the above mentioned results it was found that the right method was being used, so experiments were therefore continued alternating the percentages of ore and acid first using marcasite then pyrite and lastly chalcopyrite. These experiments showed that the marcasite gave the best results, with chalcopyrite next, while those of pyrite came last. A 3% strength sulphuric acid gave the best extraction. The following results are the final ones:

Sulphatizing Roast Kaysers Method.

Time of roast forty minutes.

Furnace-assay muffle.
Total volume of solution 100cc.
Temperature of roast at the beginning 170° C.
Temperature of roast at the finish not to exceed 300° C

Sample	Flue D.	Marcasite	Days leach.	H_2SO_4 by vol.	% CU Ex.
I	80gms.	1gm.	I	3%	93.32
2	"	"	2	"	94.64
3	"	"	3	"	99.05
4	"	"	4	"	99.38
5	"	"	5	"	99.40

Acid Consumption.

Sample	% acid consumpt.
I	I.40
2	I.6I
3	I.87
4	I.90
5	I.96

For all purposes we might say that the maximum extraction takes place at the end of the fourth day.

The exact method of this flue dust leaching as carried on in the laboratory of the Missouri School of Mines is as follows:

Method of Treatment.

A.Roasting.

The "flue dust" is given a sulphatizing roast with marcasite, the ratio by weight being about 80 (flue dust) to I (marcasite). From an analysis of the "flue dust" and marcasite, which by the way was impure, it was determined that the sulphur content of the "flue dust" was 9.075% while the marcasite ran 13.34%. It is evident from this that for the required roast 4.451bs. of S are added to the "flue dust" from the marcasite.

Roasting was carried on in the muffle of an ordinary assay furnace, hand rabbling being resorted to every few minutes. The essential factors in the roast are:

a. Time.
b. Temperature.
c. Air, or Oxygen.

The best results are obtained when the time factor is made as great as possible, assuming that the air remains the same. Or, again, the best results will be obtained by having the time factor as large as possible, speaking, of course, within practical limits. By increasing the air, the temperature remaining the same, the time will be greatly diminished without detriment to the roast.

The air factor in an assay furnace is essentially large and a thorough and complete roast of forty

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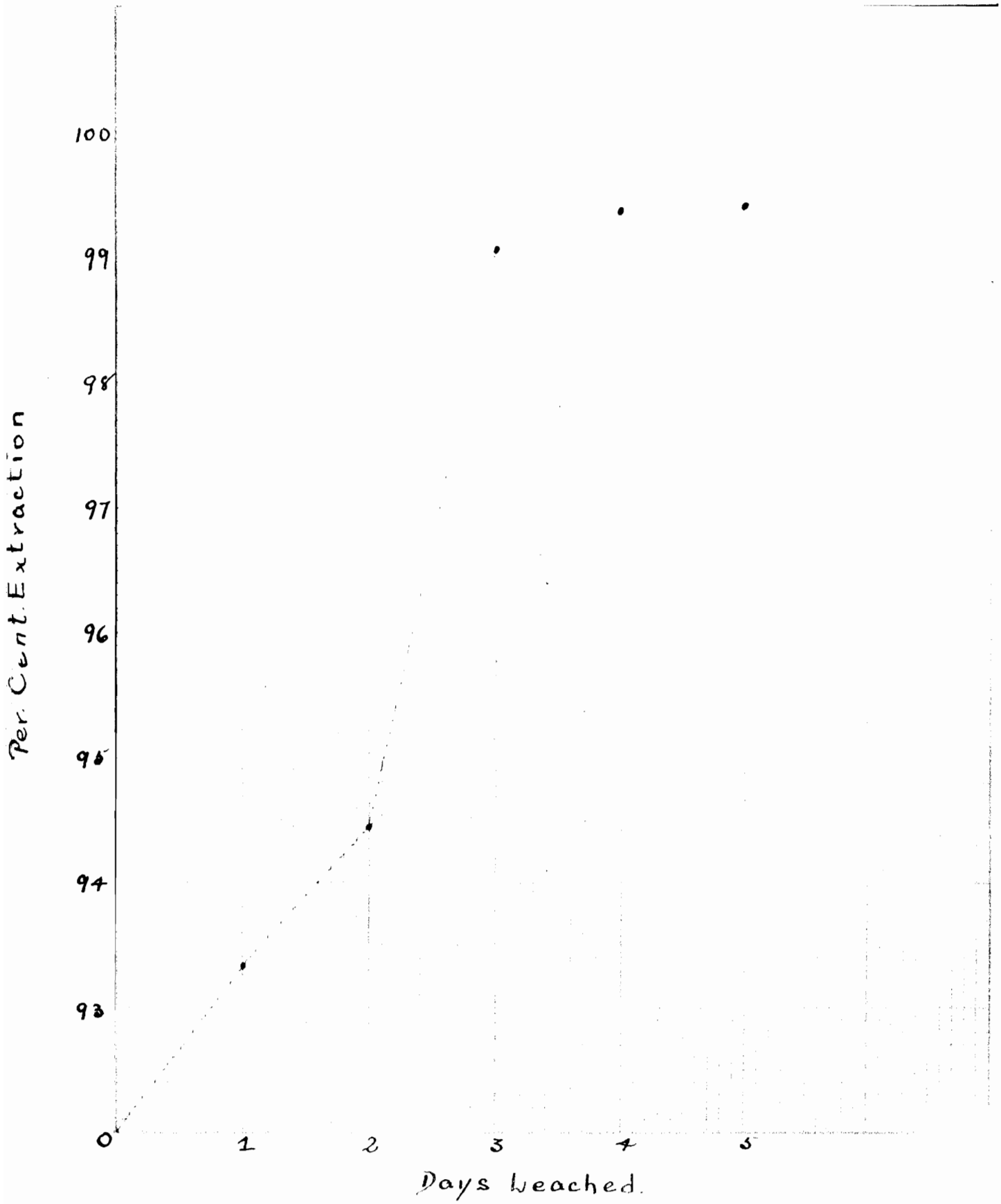


minutes was given the "flue dust", during which time the temperature was not allowed to go above 300° C. Too much emphasis can not be laid on the roast, for if the roast becomes one of oxidation the "flue dust" becomes useless for further treatment. Too low a temperature is preferable to one too high. The roasted product has a decided reddish appearamce.

A long-flame bituminous coal, if direct firing is used is best; while lighite, with its short flame and and low heating quality, is the worst.

It is desirable to bring the sulphides present to the ignition temperature as soon as possible after the ore has been introduced into the furnace. For this purpose a comparatively thin bed of "flue dust", say 2.5 to 3 in. thick, is preferable.

B. Leaching.

While still warm the desired amount of ore is transferred to a beaker having a capacity of 500cc. To this beaker is added a hot solution of water and sulphuric acid, the strength by volume of the sulphuric acid being 3%. The beaker remained unmolested until the end of the fifth day when it was found that the required extraction had taken place. For all practical purposes, however, the maximum extraction takes place at the end of the fourth day.

C. Precipitation.

Two methods were employed for precipitating Cu from the sulphate solution:

1. Scrap iron.
2. Sponge iron.

Under the adverse conditions of free acid, ferric salts, and impure scrap iron, the consumption of the iron in precipitating the copper from the sulphate solution averaged about I.5 lbs. of iron per pound of copper precipitated.

Ferrous sulphate by prolonged contact with the air is decomposed into free sulphuric acid and ferric sulphate; the former dissolves the iron, and the latter combines with it to again form ferrous sulphate.

The following chemical changes take place in precipitating with iron from a sulphate solution:

a. $CuSO_4 + Fe = Cu + FeSO_4$

If this reaction were theoretically carried out, only 88.8 parts of iron would be required to precipitate I00 parts of copper.

b. $Fe_2(SO_4)_3 + Fe = 3FeSO_4$
c. $H_2SO_4 + Fe = FeSO_4 + 2H$

The foregoing is the principle on which the copper is precipitated from the sulphate solution.

In practice the consumption ratio of iron to copper is from I;2 to I:3.

2. Sponge iron.

The sponge iron was made in the laboratory as follows. If ferric oxide, Fe_2O_2, is heated in a highly reducing atmosphere, the oxygen of the iron oxide combines with the reducing gases, and the resultant product is finely divided iron, containing more or less impurities. Great care must be used in cooling the iron to prevent reoxiditation, so that the cooling as well as the heating, must be done in the presence of reducing gases.

The disadvantages found in the use of the sponge iron consisted in the trouble required to make it, and to the fact, that continuous stirring is required. This in practice will necessitate some kind of a mechanical agitator.

In precipitating the copper from cuprous liquors by means of metallic iron, the spent solutions are regenerated by forcing heated air thru them.

Both these methods gave a high extraction of copper, 99% plus, but preference should be given to the scrap iron as it is the most convenient to use.

Conclusion.

The following tables show the comparative cost between the process of treating "flue dust" by leaching and by the reverberatory furnace.

The essential costs of leaching have been taken from material furnished by the leading engineering periodicals and text books, and it is to be noticed that the price for treating a mixture of the "flue dust" and magnesite ore is about two cents per pound cheaper than that given by some of the most economical processes.

Estimate of Cost of Leaching Flue Dust.

Labor, assaying, and superintendance (10 men)----	$0.225/ton.
Roasting----------	$0.300 "
Acid (16 lbs. at $0.05 per lb.)----------	$0.080 "
Iron for precipitation----------	$0.700 "
Cost of refining at $12.50 per ton of Cu.-----	$0.560 "
Depreciation and general expenses----------	$0.350 "
Power----------	$0.270 "
Shipping----------	$0.160 "
Total cost per ton of ore treated	$2.645

Cost per lb. of Cu $0.0297.

Estimate of Cost of Treatment by Reverberatory.

Labor, assaying, and superintendance (10 men)---	$0.225/ton.
Reverberatory treatment----------	$1.850 "
Cost of refining at $12.50 per ton of Cu-----	$0.560 "
Depreciation and general expenses----------	$0.350 "
Power----------	$0.270 "
Shipping----------	$0.160 "
Total cost per ton of ore treated	$3.415

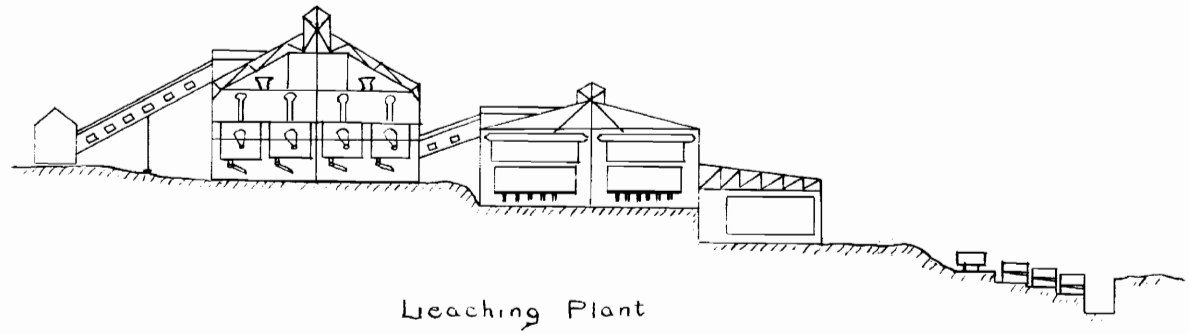
Cost per lb. of Cu $0.0383.

A suggestion for a 200 ton mill to handle "flue dust" by the above method.

The following equiptment will be necessary:

8 Leaching tanks 20' diam. 8' high.
6 Brown muffle furnaces 35 ton capacity each.
4 Solution tanks 20' diam. 8' high.
4 Precipitating boxes 3' 5' 100'.
1. Settler 3' 8'' 8' 50'.
6 Ore bins 50' 7' 12' total capacity 2000 tons.
Lead acid tank.

Electrolytic precipitation being in cases cheaper, experiments along this line might be encouraged.



Leaching Plant